

PATENT ABSTRACTS OF JAPAN

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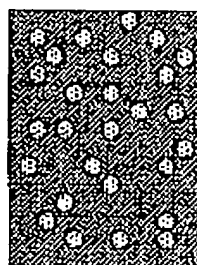
(54) MANUFACTURING METHOD OF NICKEL-HYDROGEN STORAGE BATTERY AND METALLIC ALLOY FOR THE HYDROGEN STORAGE NEGATIVE ELECTRODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nickel-hydrogen storage battery wherein the elevation of the inner pressure is restrained by the increase in the water repellency of the surface of an alloy for a hydrogen storage electrode and the improvement is made in hydrogen gas absorption capacity of alloy for the hydrogen storage alloy.

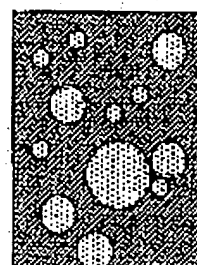
SOLUTION: A hydrogen storage alloy negative electrode is manufactured by filling or coating support body with a paste whose main component is powder of an alloy for hydrogen storage, and a nickel-hydrogen storage battery is manufactured using a hydrogen storage alloy negative electrode wherein the surface of the hydrogen storage alloy negative electrode is coated with a solution in which a water repellant fluororesin is mixed with an organic solvent and the fluororesin is made to be in a dispersion state in the organic solvent, while giving ultrasonic refractions.

実施例の負極表面



表面状態良好

比較例の負極表面



空隙多量

① FEP
② 大粒

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the hydrogen storing metal alloy negative electrode which applies to said organic solvent the solution which made said fluoro-resin the distributed condition on the front face of said hydrogen storing metal alloy negative electrode while filling up with or plastering a base material with the paste which uses hydrogen storing metal alloy powder as a principal component, producing a hydrogen storing metal alloy negative electrode, mixing the fluoro-resin powder and organic solvent which are water repellent and adding supersonic vibration.

[Claim 2] Supersonic vibration is the manufacture approach of the hydrogen storing metal alloy negative electrode according to claim 1 which are the frequency of 5-40kHz, and the amplitude of 40-100 micrometers.

[Claim 3] The amount of fluoro-resin powder is the manufacture approach of the hydrogen storing metal alloy negative electrode according to claim 1 which is 4 - 15% to an organic solvent.

[Claim 4] The amount of the fluoro-resin powder applied to the front face of a hydrogen storing metal alloy negative electrode is the manufacture approach of the hydrogen storing metal alloy negative electrode according to claim 1 which is 0.10 - 2.0 mg/cm².

[Claim 5] The nickel-hydrogen battery by which it is the nickel-hydrogen battery which consists of the positive electrode which makes nickel hydroxide a subject, a hydrogen storing metal alloy negative electrode, a separator, and the electrolytic solution, and 5-100-micrometer fluoro-resin powder is applied to the front face of said hydrogen storing metal alloy electrode in the state of distribution.

[Claim 6] The amount of the fluoro-resin powder applied to the front face of a hydrogen storing metal alloy negative electrode is a nickel-hydrogen battery according to claim 5 which is 0.10 - 2.0 mg/cm².

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of a nickel-hydrogen battery and the hydrogen storing metal alloy negative electrode used for it.

[0002]

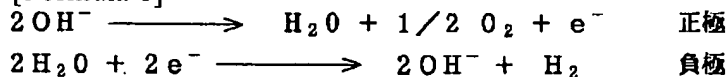
[Description of the Prior Art] As a battery well used from the former, a nickel cadmium battery or a lead accumulator is mentioned. By the way, I hear that it may be more nearly lightweight than these cells, and may become a high energy consistency by high capacity, and the nickel-hydrogen battery equipped with the hydrogen absorption negative electrode using the hydrogen storing metal alloy as a negative-electrode ingredient attracts attention in recent years.

[0003] Generally, as shown in JP,61-66366,A, the hydrogen storing metal alloy negative electrode used for the negative electrode of this alkaline battery kneads a binder and hydrogen storing metal alloy powder, such as polytetrafluoroethylene and polyethylene oxide, produces a paste, and both sides of axes, such as a punching metal, are plastered with said paste, it dries to them, and it is produced. In this way, the produced hydrogen absorption negative electrode is held in a cell sheathing can in the condition of having made the separator intervening between the sintering type nickel positive electrodes used for the nickel cadmium battery, and having wound around the curled form, and a nickel-hydrogen battery is constituted.

[0004] Here, by the above-mentioned nickel-hydrogen battery, as it is shown in a positive electrode and a negative electrode shows to a degree type at the time of overcharge, a generation-of-gas reaction occurs, and cell internal pressure rises. Especially, in boosting charge, this pressure buildup becomes remarkable.

[0005]

[Formula 1]



[0006] So, the approach of applying a negative electrode to the water solution which made PVA distribute fluororesin powder as an example of manufacture which prepares water-repellent resin in a hydrogen storing metal alloy negative-electrode front face is proposed by JP,2-291665,A.

[0007]

[Problem(s) to be Solved by the Invention] In case the solution which distributed fluororesin powder to the organic solvent is applied to the front face of a hydrogen storing metal alloy negative electrode, in the magnitude of the particle of the fluororesin powder in a solution. However, since variation is large, The spreading unevenness to plugging and the negative electrode of a spreading nozzle occurs, and since the circumference of the liquid of the electrolytic solution gets worse, if the front face of the hydrogen storing metal alloy negative electrode with which fluororesin powder is unevenly distributed constitutes a nickel-hydrogen battery, using this negative electrode, the problem that that cell internal pressure rises

will arise.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention filled up with or plastered the base material with the paste which uses hydrogen storing metal alloy powder as a principal component, the hydrogen storing metal alloy negative electrode was produced, and the solution which made the fluororesin the distributed condition at the organic solvent was considered as the manufacture approach of the hydrogen storing metal alloy negative electrode applied to the front face of a hydrogen storing metal alloy negative electrode, adding supersonic vibration, while mixing the fluororesin powder and organic solvent which are water repellent.

[0009] The water repellence of a plate increases and it aims at improvement in the hydrogen gas absorption of a hydrogen storing metal alloy for this to aim at the increment in the specific surface area of the fluororesin applied to the hydrogen storing metal alloy plate. Moreover, it aims at reducing plugging and the spreading unevenness of a nozzle.

[0010]

[Embodiment of the Invention] Invention of this invention according to claim 1 fills up with or plasters a base material with the paste which uses hydrogen storing metal alloy powder as a principal component, produces a hydrogen storing metal alloy negative electrode, and it considers the solution which made said fluororesin the distributed condition at said organic solvent as the manufacture approach of the hydrogen storing metal alloy negative electrode applied to the front face of said hydrogen storing metal alloy negative electrode, adding supersonic vibration, while mixing the fluororesin powder and organic solvent which are water repellent.

[0011] Since fluororesin powder can prevent getting it blocked in a nozzle and is applied to homogeneity on the front face of a hydrogen storing metal alloy negative electrode by this, water repellence increases and improvement in the hydrogen gas absorption of a hydrogen storing metal alloy can be aimed at.

[0012] Moreover, as for the above-mentioned supersonic vibration, it is desirable that they are the frequency of 5-40kHz and the amplitude of 40-100 micrometers. Dispersion effect with a frequency sufficient with 5kHz and the amplitude of 40 micrometers is not acquired. If a frequency exceeds 40kHz and the amplitude of 100 micrometers, the generator of a big supersonic wave is required and is not realistic.

[0013] Furthermore, while water-repellent effectiveness is acquired with the amount of fluororesin powder being 4 - 15% to the above-mentioned organic solvent, since it can apply to homogeneity, it is desirable.

[0014] If it is desirable that it is 0.10 - 2.0 mg/cm² as for the amount of the fluororesin powder applied to the front face of the above-mentioned hydrogen storing metal alloy negative electrode and the amount of this fluororesin powder is 0.10mg [/] less than 2 cm, its water-repellent effectiveness is not enough, and since it will be hard coming to absorb the electrolytic solution and resistance of a hydrogen storing metal alloy negative electrode will go up if [than 2.0 mg/cm²] more, it is not desirable further again.

[0015]

[Example] Hereafter, the example of this invention is explained.

[0016] The sintering type nickel substrate was filled up with the nickel hydroxide which is an active material, and the positive electrode 1 was produced.

[0017] The hydrogen storing metal alloy powder which ground mechanically the hydrogen storing metal alloy by which an alloy presentation is expressed with Mm3.55Mn0.4aluminum0.3Co.75 (Mm is the mixture of rare earth) so that it might become the mean particle diameter of 30 micrometers underwater with a wet ball mill was produced. It rinsed until pH of the rinsed water which carried out immersion stirring for 60 minutes became ten or less in this alloy powder and the potassium-hydroxide water solution of specific gravity 1.30 warmed at 80 degrees C of this weight, and the hydrogen storing metal alloy powder slurry was obtained.

[0018] Water was mixed as a thickener to the weight 100 of this alloy powder slurry, having used [the carboxymethyl cellulose] the styrene-butadiene copolymer as a binder as 0.8 % of the weight and a

dispersion medium for carbon black 0.3% of the weight as an electric conduction agent 0.15% of the weight, and the paste was produced.

[0019] After plastering with this paste the conductive support surface which consists of a punching metal, desiccation and pressurization were performed and the negative electrode 2 was obtained.

[0020] On the front face of the obtained hydrogen storing metal alloy negative electrode 2, thus, 5.89% of the weight of a tetrafluoroethylene-hexafluoropropylene copolymer (It is hereafter called FEP.) The condition of having distributed the FEP powder in a solution while producing the solution which added powder to the ethanol which is a dispersion medium, stirring this solution and adding supersonic vibration on conditions with an amplitude [of 80 micrometers], and a frequency of 20kHz (the particle size of the FEP powder at this time was 5-72 micrometers.) It sprayed in the amount of 0.20 mg/cm², 0.41 mg/cm², and 0.61 mg/cm², and three kinds, the negative electrode 2-1 of this invention, 2-2, and 2-3, were produced.

[0021] Thus, each of a negative electrode 2-1 to 2-3 and the sintering type nickel positive electrode 1 which were produced It is made to wind through the separator 3 which consists of a nonwoven fabric made from polypropylene. After producing the spiral electrode group 4, containing this in the cell case 5 and pouring in 30% of the weight of a potassium-hydroxide water solution as the alkali electrolytic solution in this cell case 5, the upper part of the cell case 5 is sealed with the obturation plate 6. The cylinder closed mold nickel-hydrogen batteries A1 and A2 in the example of this invention of nominal capacity 750mAh and A3 were produced in AAA size.

[0022] (Example of a comparison) In addition to the ethanol which is a dispersion medium, 5.89% of the weight of FEP powder was stirred on the front face of the negative electrode 2 produced in the above-mentioned example, the solution (the particle size of the FEP powder at this time was 20-150 micrometers.) was produced on it, this was sprayed on it in the amount of 0.20 mg/cm², 0.41 mg/cm², and 0.61 mg/cm², and three kinds, the negative electrode 7-1 of the example of a comparison, 7-2, and 7-3, were produced.

[0023] The nickel-hydrogen battery B1 of the example of a comparison considered as the same configuration as the above-mentioned example, B-2, and B3 were produced except having used each of the negative electrode 7-1 of the example of a comparison, 7-2, and 7-3.

[0024] (Experiment 1) The cells A1 and A2 of an example, the cell B1 of A3 and the example of a comparison, B-2, and each cell of B3 measured cell internal pressure, having opened the hole in the pars basilaris ossis occipitalis of a case beforehand, having attached the pressure sensor for internal pressure measurement in this pore, and performing charge with a 750mA current after 2-hour neglect under a 45-degree C ambient atmosphere for 1.2 hours. This result is shown in (Table 1).

[0025]

[Table 1]

	実施例			比較例		
	A 1	A 2	A 3	B 1	B 2	B 3
内圧上昇割合 (B1を100 とした場合)	55.5	50.0	45.3	100	74.4	74.4

[0026] If the coverage of the example [an example and] of a comparison of FEP powder increases, cell internal pressure will fall, so that clearly from (Table 1). Moreover, if an example is compared with the example of a comparison, when the coverage of FEP powder is the same, the cell internal pressure of an example becomes lower than that of the example of a comparison, and the cell of an example is better than the cell of the example of a comparison.

[0027] This is considered that cell internal pressure became high since the FEP powder applied to the front face of the negative electrode 2 in the example was distributed by homogeneity, FEP powder condensed on the front face of the negative electrode 7 in the example of a comparison to cell internal pressure being low good since water repellence is good, it changed into the uneven condition and water

repellence was spoiled as shown in drawing 1 , and it became not good.

[0028] Furthermore, this is understood also from it having been 20-200 micrometers, when the particle size of the FEP powder which is 5-90 micrometers and is similarly located in the front face of a negative electrode 7 if the particle size of the FEP powder currently distributed on the front face of the negative electrode 2 of an example with the SEM photograph is measured is measured.

[0029] In the above-mentioned example, although FEP powder was used for the front face of a negative electrode 2 as water repellent, even if it uses fluororesin powder, such as PTFE, the same effectiveness is acquired.

[0030] Moreover, in the above-mentioned example, although the amount of FEP powder was made into 5.89 % of the weight to the organic solvent as water repellent on the front face of a negative electrode 2, if it is 4 - 15% of the weight of the range, the same effectiveness will be acquired as the amount.

[0031] Furthermore, although the range of the particle size of the FEP powder currently distributed on the negative-electrode front face was 5-90 micrometers in the above-mentioned example, the range where this particle size is desirable is 5-100 micrometers.

[0032] Although the amount of the FEP powder applied to the front face of the negative electrode 2 of the above-mentioned example was the range of 0.20 - 0.61 mg/cm², as an amount of FEP powder, the range of 0.10 - 2.0 mg/cm² is desirable further again.

[0033]

[Effect of the Invention] As mentioned above, by according to this invention, carrying out pulverization of the fluororesin which the organic solvent was made to distribute to the front face of a hydrogen storing metal alloy electrode, and applying it to it, the increment in the specific surface area of a fluororesin being aimed at and the water repellence of a plate increase, improvement in the hydrogen gas absorption of a hydrogen storing metal alloy is attained, and a cell internal pressure rise can be controlled, and the advantageous effectiveness that plugging and the spreading unevenness of a nozzle can be reduced is acquired.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the surface state of the negative electrode in the example of this invention, and the negative electrode of the example of a comparison

[Drawing 2] The half-decision side Fig. of the nickel-hydrogen battery in the example of this invention

[Description of Notations]

- 1 Positive Electrode
- 2 Negative Electrode
- 3 Separator
- 4 Electrode Group
- 5 Cell Case
- 6 Obturation Plate
- 7 Negative Electrode of Example of Comparison

[Translation done.]